REPORT DOCUMENTATION PAGE

Form Approved OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE:	3. REPORT TYPE AND DATES COVERED Final Report 15-Feb-2005 - 14-Aug-2006

4. TITLE AND SUBTITLE

First Principles and Multiscale Modeling of Spallation and Erosion of Gun Tubes

5. FUNDING NUMBERS

W911NF0510053

6. AUTHORS

Emily A. Carter

8. PERFORMING ORGANIZATION REPORT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

Princeton University
Office Of Research & Project Administration
The Trustees of Princeton University
Princeton, NJ 08544 -0036

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER

47550-CH.1

11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for Public Release; Distribution Unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The abstract is below since many authors do not follow the 200 word limit

14. SUBJECT TERMS

gun barrel erosion, steel, density functional theory, multiscale modeling

15. NUMBER OF PAGES

Unknown due to possible attachments

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev .2-89)
Prescribed by ANSI Std.
239-18 298-102

Report Title

First Principles and Multiscale Modeling of Spallation and Erosion of Gun Tubes

ABSTRACT

This presents the final report for 1.5 years of research at Princeton by the PI and her group on the gun tube erosion problem. During this period, a new quantum mechanics simulation tool was developed and interfacial materials chemistry aspects of the gun tube erosion problem were investigated. Specifically, ultrasoft spin-dependent pseudopotential density functional theory (DFT) was developed, which provides an accurate and efficient ab initio description of magnetic transition metals such as Fe. DFT was used to evaluate the structure and stability of a multilayer protective coating for steel comprised of MoSi2 and SiO2, as an alternative for the usual chrome coating. Properties of the Cr/Fe interface were also calculated and the origin of the stability of the chrome coating identified. Pathways for common propellants CO and H2S adsorption, diffusion, and dissociation on Fe and Fe alloy surfaces were also investigated. These findings were reported in five journal publications, with two more publications in press.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Donald F. Johnson, D. E. Jiang, and E. A. Carter, “Structure, Magnetism, and Adhesion at Cr/Fe Interfaces from Density Functional Theory,” Surface Science, in press (2006).
D. E. Jiang and E. A. Carter, “Prediction of a Highly Activated State of CO Adsorbed on an Al/Fe(100) Bimetallic Surface,” J. Phys. Chem., in press (2006).
V. Cocula, C. J. Pickard, and E. A. Carter, “Ultrasoft Spin-Dependent Pseudopotentials,” J. Chem. Phys., 123, 214101 (2005).
D. E. Jiang and E. A. Carter, "Effects of Alloying on the Chemistry of CO and H?S on Fe Surfaces," J. Phys. Chem. B, 109, 20469-20478 (2005).
D. E. Jiang and E. A. Carter, “First Principles Study of the Interfacial Adhesion between SiO2 and MoSi2,” Phys. Rev. B, 72, 165410 (2005).
D. E. Jiang and E. A. Carter, “Prediction of Strong Adhesion at the MoSi2/Fe Interface,” Acta Materialia, 53, 4489 (2005).
D. E. Jiang and E. A. Carter, “First principles study of H2S adsorption and dissociation on Fe(110),” Surf. Sci., 583, 60 (2005).

Number of Papers published in peer-reviewed journals: 7.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

12 Invited Lectures at Conferences Delivered by the P.I.

July 13, 2006 "Quantum-Based Simulations of Degradation and Protection of Steel," at the Foundations of Molecular Modeling and Simulation: Tools for Innovations Conference, Blaine, Washington.

May 24, 2006 "Status and Challenges in Modeling Nanomaterials and Surface Chemistry," at the Chem-Semi Nanotechnology Modeling Workshop at the National Institute of Standards and Technology, Gaithersburg, Maryland.

May 17, 2006 "Spin-Dependent Pseudopotential Theory for Magnetic Materials," at the 2006 Program in Applied and Computational Mathematics Conference at Princeton University, Princeton, NJ.

April 4, 2006"Coupling Quantum and Continuum Mechanics for Insights into Mechanical Response of Materials," at the Multi-scale modelling: Electrons, Molecules and (Bio)Materials Conference at the Royal Netherlands Academy of Arts and Sciences, Amsterdam, The Netherlands.

Jan. 18, 2006"Materials Failure and Design Insights from Quantum-Based Simulations," talk at the Computational Techniques for Nano-scale Physics Symposium at the GE Global Research Center, Niskayuna, NY.
Nov. 21, 2005 "Stressed Out Materials: Learning From Failure From the Bottom Up," Plenary Lecture at the 13th Brazilian Symposium of Theoretical Chemistry, Sao Pedro, Brazil.

Oct. 21, 2005 "Multiscale Modeling of the Mechanical Response of
Materials: Coupling of Chemistry to Mechanics," talk at the 2nd ETHZ School in Multiscale Modelling and Simulation at the Swiss Federal Institute of Technology, in Zurich, Switzerland.

June 15, 2005 "Quantum-Based Multiscale Modeling of Materials," at the ACS PRF Summer School on Computation, Simulation, and Theory in Chemistry, Chemical Biology, and Materials Chemistry, Park City, Utah.

June 15, 2005 "Materials Applications of Periodic Density Functional Theory: Corrosion & Protection of Metals," at the ACS PRF Summer School on Computation, Simulation, and Theory in Chemistry, Chemical Biology, and Materials Chemistry, Park City, Utah.

June 15, 2005 "Spin-Dependent Pseudopotential Theory for Open-Shell and Magnetic Systems," at the ACS PRF Summer School on Computation, Simulation, and Theory in Chemistry, Chemical Biology, and Materials Chemistry, Park City, Utah.

Mar. 16, 2005 "Design of strongly interacting metal-ceramic and ceramic-ceramic interfaces," at the 229th ACS National Meeting, San Diego, CA.

Feb. 16, 2005 "Surface and Interface Chemistry Related to Steel Erosion," at the 2005 Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, CA.

5 Contributed Talks Delivered at Conferences by Graduate Students

Aug. 29, 2005 "Chemistry of iron surfaces and interfaces from first principles," poster at the the 230th ACS National Meeting, Washington, DC (presented by De-en Jiang).

July 17, 2005 "Magnetic Structure and Adhesion of the Fe(100)/Cr(100) And Fe(110)/Cr(110) Interfaces," poster at the American Conference on Theoretical Chemistry, Los Angeles, CA (presented by Donald Johnson).

May 2, 2005 "Structure, Bonding, and Adhesion of MoSi2/Fe and SiO2/MoSi2 from First Principles," talk at the International Conference On Metallurgical Coatings And Thin Films, San Diego, CA (presented by De-En Jiang).

Mar. 25, 2005 "Structure, bonding and adhesion of MoSi?/Fe and SiO?/MoSi? from first principles," talk at the APS March Meeting, Los Angeles, CA (presented by De-En Jiang).

Feb. 14, 2005 "Prediction of a Highly Activated State of CO on an Ultrathin Al film on Fe(100)," poster at the Gordon Research Conference on Chemical Reactions at Surfaces, Ventura, CA (presented by De-En Jiang).

Number of Presentations: 17.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts): 0

(d) Manuscripts

Number of Manuscripts: 0.00

Number of Inventions:

Graduate Students

NAME	PERCENT_SUPPORTED	
De-en Jiang	1.00	No
Donald Johnson	1.00	No
FTE Equivalent:	**2.00**	
Total Number:	**2**	

Names of Post Doctorates

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Emily A. Carter	0.06	No
FTE Equivalent:	**0.06**	
Total Number:	**1**	

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED
FTE Equivalent:	
Total Number:	

Names of Personnel receiving masters degrees

NAME
Total Number:

Names of personnel receiving PHDs

NAME	
De-en Jiang	No
Total Number:	**1**

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Sub Contractors (DD882)

Inventions (DD882)

FINAL REPORT

TO THE

U. S. ARMY RESEARCH OFFICE

NOVEMBER 2006

On the grant entitled

"First Principles and Multiscale Modeling of Spallation and Erosion of Gun Tubes"

GRANT NO. W911NF0510053

PROJECT PERIOD: 2/15/2005 to 8/14/2006

EMILY A. CARTER
PRINCIPAL INVESTIGATOR

Department of Mechanical and Aerospace Engineering
Princeton University
Princeton, NJ 08544-5263

Statement of the Problem Studied

Increasing the service lifetime of military machinery will improve logistics in the field (less down-time due to maintenance or replacement) and will free up resources for other pressing needs. To this end, the Army would like to enhance the lifetime of gun barrels, which are limited currently by steel erosion. As it is not possible to determine the erosion mechanisms in real time experimentally *in situ*, computer simulations can help elucidate those mechanisms and ultimately extend gun barrel lifetime by suggesting new ways to stop the erosion.

In the past 1.5 years, a new quantum mechanics simulation tool was developed and interfacial materials chemistry aspects of the gun tube erosion problem were investigated. Specifically, ultrasoft spin-dependent pseudopotential density functional theory (DFT) was developed, which provides an accurate and efficient ab initio description of magnetic transition metals such as Fe and Cr. DFT was used to evaluate the structure and stability of a multilayer protective coating for steel comprised of $MoSi_2$ and SiO_2, as an alternative for the usual chrome coating. Properties of the Cr/Fe interface were also calculated and the origin of the stability of the chrome coating identified. Pathways for CO and H_2S adsorption, diffusion, and dissociation on Fe and Fe alloy surfaces were also investigated, in order to understand the surface chemistry of common propellant byproducts. These findings were reported in five journal publications, with two other publications in press. Note that this grant is of shortened duration as it is the latter half of a grant that originated when the P.I. was at UCLA instead of Princeton. Only those results published since the continuation grant was initiated at Princeton are discussed here, and the reader is referred to the earlier final report submitted for the research done under the earlier part of the grant at UCLA.

Summary of the Most Important Results

The most important findings during tenure of this grant are described below, where the references refer to the publication list at the end of this section. We first discuss the new DFT pseudopotential method we developed and how robustly it describes properties of magnetic transition metals such as iron. Then we review how DFT was used to elucidate the initial stages of sulfidization and carburization of steel, and to quantify the stability of a potential alternative coating for steel. We verified that H_2S dissociates readily on Fe, thereby providing both sulfur to the surface (the precursor to FeS) and hydrogen that can subsequently enter and embrittle steel. We then went on to consider alloy pretreatments of the Fe surface as a strategy for inhibiting deleterious surface chemistry, focusing on FeAl and Fe_3Si. We found that neither could adequately inhibit H_2S dissociation reactions, while Si alloying could help prevent CO dissociation (the precursor to carbide formation). Al alloying of steel has the opposite effect desired, namely to catalyze CO dissociation. Given our failure to find a successful alloy pretreatment strategy that would simultaneously prevent reactions of multiple propellant byproducts with steel surfaces, we turned our attention to protective coating design. The origin of the Cr/Fe interfacial strength was pinpointed – namely strong spin-correlations and d-d bonding across the interface combined with near perfect lattice

matching are responsible for the excellent adhesion of Cr to Fe. We then examined $MoSi_2$ and its oxide scale SiO_2 as a possible alternative less toxic protective coating for steel. We found that the ideal strength of this multilayer coating is lower but perhaps competitive to chrome, suggesting it may be a useful coating pursue, particularly in a composite form, perhaps coupled to a thermal barrier coating on top of the silica scale, such as yttria-stabilized zirconia.

I. Advances in Spin-Dependent Pseudopotential Theory

Since the primary components of a gun tube are steel and chrome, i.e. Fe and Cr, both of which are magnetic (Fe is ferromagnetic, Cr is antiferromagnetic), it is critical to describe their magnetic properties accurately, since these may affect other properties such as structure and energetics. The standard DFT pseudopotential method often fails to describe magnetic transition metals because the conventional pseudopotentials are spin-averaged. Our spin-dependent pseudopotential theory is constructed to give the correct pseudopotential limits for spin-neutral and fully spin-polarized atoms, and works between those limits by scaling the fully polarized potential by the spatially varying net spin polarization. It does so without added parameters, while providing a more flexible description that self-consistently adapts to the local environment. During the term of this grant, we reformulated our earlier incarnations of the spin-dependent pseudopotential theory to work within the computationally advantageous ultrasoft pseudopotential formalism, showing that we retain the previously demonstrated accuracy of the norm-conserving pseudopotential approach, while dramatically lowering the cost of the calculation [1]. We showed, for example, this ultrasoft spin-dependent pseudopotential theory reproduces all-electron density functional theory results for many different phases and magnetic structures of iron, including the correct magnetic ground state and transition as a function of compression and tension for austenite (fcc Fe), a material phenomenon where conventional ultrasoft pseudopotential theory fails.

II. Applications of Periodic DFT to the Gun Tube Erosion Problem

A. Interaction of CO and H_2S with Fe and Fe alloy surfaces

H_2S is a common byproduct of the propellants used in military guns and may be the source of the FeS observed by electron microscopy in eroded gun tubes, as well as the source of hydrogen that may cause hydrogen embrittlement of the steel. We used DFT to characterize H_2S and HS adsorption, diffusion, and dissociation on the Fe(110) surface. H_2S is predicted to weakly adsorb via a sigma-donor bond on the short bridge (SB) or long bridge (LB) site, with a binding energy of no more than 0.50 eV. The H_2S diffusion barrier is predicted to be small (~0.1 eV). By contrast to H_2S, HS is predicted to be strongly chemisorbed on Fe(110), with the S atom in the highest coordination site and the HS bond oriented perpendicular to the surface, due to charge transfer from the surface to S p-orbitals. Isolated S atoms also are predicted to bind strongly to the LB sites of Fe(110), with bridge sites found to be transition states for S hopping between neighboring LB sites. HS is more strongly absorbed than H_2S due to its ability to form a

primarily ionic bond, and S is the most strongly bound of all due to its ability to form two polar covalent bonds. The minimum energy paths for H_2S and HS dehydrogenation involve rotating an H atom towards a nearby surface Fe atom, with the S-H bonds breaking on the top of only one Fe atom. The barriers to break the first and second S-H bonds in H_2S are low: 0.1 eV and zero on Fe(110), respectively, suggesting deposition of S on Fe(110) via H_2S is kinetically and thermodynamically facile, consistent with experiments [2].

We then considered whether alloying the steel surface might be able to inhibit damaging surface reactions by raising the barriers to molecular dissociation of CO and H_2S [3]. We chose to examine Fe-Al and Fe-Si alloys because they are the only binary Fe alloys with favorable thermo-mechanical properties that might allow them to survive under the harsh conditions of a gun barrel firing. We had already determined that H_2S dissociates on pure iron surfaces much more easily than CO does. Although FeAl surfaces raise the barriers for H_2S dissociation, they significantly lower the barriers for CO dissociation. On the other hand, Fe_3Si surfaces raise the barriers for CO dissociation, but they are as vulnerable as Fe surfaces to H_2S dissociation. Our findings suggest that alloying steel with Al or Si is unlikely to simultaneously increase its resistance to the initial stages of chemical degradation by CO and H_2S. However, it is possible that alloying the outer few microns of steel with Al or Si still might prove useful, if the barriers to diffusion of C and H might be significantly raised by alloying. We are currently investigating this possibility.

The fact that alloying Fe with Al lowered dramatically the barrier for CO dissociation made us wonder about the possibility of an industrial spin-off, namely the use of some FeAl bimetallic surface as a potential low temperature catalyst for CO conversion. We therefore investigated [4] CO adsorption, diffusion, and dissociation energetics on a monolayer of Al covering Fe(100) [Al/Fe(100)]. We predict a weakly chemisorbed state of CO to exist on Al/Fe(100), with CO adsorbing on the fourfold hollow site in a very tilted fashion. This state is predicted to have an extremely low CO stretching frequency of only 883 cm^{-1}, indicating a dramatically weakened CO bond relative to gaseous CO, even though the molecule is predicted to bind to Al/Fe(100) quite weakly. We predict that dissociation of CO starting from this weakly adsorbed state has a barrier of only ~0.35 eV, which is ~0.70 eV lower than that on Fe(100). To understand how the underlying substrate changes the electronic properties of the supported Al monolayer, we compare CO adsorption on Al/Fe(100) to its adsorption on analogous pure Al(100) surfaces. This highly activated yet weakly bound state of CO suggests that Al/Fe(100) could be an effective low temperature bimetallic catalyst for Fisher-Tropsch type chemistry.

B. First Principles Exploration of Alternative Protective Coatings for Steel

In addition to examining failure mechanisms for gun tube erosion, we investigated possible alternative protective coatings for gun tubes. Currently, steel gun tubes are coating with chromium, which has two problems. One is that the Cr layer cracks and reactive gases reach the steel, leading to steel erosion. The second is that the

electroplating process that produces Cr coating on steel unfortunately also produces carcinogenic Cr(VI), an environmental hazard. As a result, the Army is looking for alternative “green” (environmentally friendly) coatings.

Our focus for coatings has been on ceramic materials, since they exhibit low thermal conductivity and high melting points, both of which are crucial in the gun firing environment. We recently examined with DFT the Cr/Fe (100) and (110) interfaces, and predicted that the ideal work of adhesion of Cr to Fe is ~5.4 J/m^2 for both interfaces, which is much stronger than any other coating we have examined to date [5]. This anomalously strong adhesion is partly due to the lack of strain (<1%), but is primarily due to significant spin correlations between antiferromagnetic Cr and ferromagnetic Fe and the attendant strong d-d bonding that results. The advantages of Cr are clear, and will be hard to match.

We evaluated $MoSi_2$ as a possible coating, because in addition to favorable thermal properties, it has the potential to be corrosion-resistant by forming a silica scale. We found that $MoSi_2$ strongly adheres to Fe, with an ideal work of adhesion of ~3.9 J/m^2 for two low-index, low-strain interfaces. This value will be a lower bound to measured adhesion energies, since the latter will be larger due to plasticity. This ideal adhesion energy for a ceramic coating to Fe is much stronger than predicted earlier by us for ZrC and TiC. We attribute this stronger adhesion to increased covalent interfacial bonding for $MoSi_2$/Fe compared to metal carbide/Fe interfaces (where metallic bonding plays a larger role), as evidenced by the rearrangement of electron density and the character of the local density of states upon formation of the interface [6].

The silica scale that forms on $MoSi_2$ should help protect $MoSi_2$ against high-temperature corrosive gases. We therefore examined the interface between SiO_2 (in the cristabolite form, used as a model for amorphous silica) and $MoSi_2$ [7]. We find that the interfacial bonding is localized, as evidenced by an ideal adhesion energy that changes only slightly with the thickness of the SiO_2 layer. Moreover, the adhesion energy displays a relatively large (0.40 J/m^2) variation with the relative lateral position of the SiO_2 and $MoSi_2$ lattices due to changes in Si-O bonding across the interface. The most stable interfacial structure yields an ideal work of adhesion of 5.0 J/m^2, indicating extremely strong adhesion. Local densities of states and electron density difference plots demonstrate that the interfacial Si-O bonds are covalent in character. Mo-O interactions are not found at the SiO_2/$MoSi_2$ interface investigated here. Our work predicts that the SiO_2 scale strongly adheres to $MoSi_2$, and further supports the potential of $MoSi_2$ as a high-temperature structural material and coating. Indeed, it is important to create this silica scale by deliberate oxidative pretreatment at high temperatures (e.g., 1200 ^oC), in order to suppress oxidatively-induced fracture of $MoSi_2$ that may occur below 600 ^oC.

Publications Sponsored by ARO

1. V. Cocula, C. J. Pickard, and E. A. Carter, “Ultrasoft Spin-Dependent Pseudo-potentials,” J. Chem. Phys. **123**, 214101 (2005).

2. D. E. Jiang and E. A. Carter, “First principles study of H_2S adsorption and dissociation on Fe(110),” Surf. Sci. **583**, 60 (2005).

3. D. E. Jiang and E. A. Carter, "Effects of Alloying on the Chemistry of CO and H_2S on Fe Surfaces," J. Phys. Chem. B **109**, 20469 (2005).

4. D. E. Jiang and E. A. Carter, “Prediction of a Highly Activated State of CO Adsorbed on an Al/Fe(100) Bimetallic Surface,” J. Phys. Chem., in press (2006).

5. D. F. Johnson, D. E. Jiang, and E. A. Carter, “Structure, Magnetism, and Adhesion at Cr/Fe Interfaces from Density Functional Theory,” Surface Science, in press (2006).

6. D. E. Jiang and E. A. Carter, “Prediction of Strong Adhesion at the $MoSi_2$/Fe Interface,” Acta Materialia **53**, 4489 (2005).

7. D. E. Jiang and E. A. Carter, “First Principles Study of the Interfacial Adhesion between SiO_2 and $MoSi_2$,” Phys. Rev. B **72**, 165410 (2005).

Participating Scientific Personnel (*indicates those supported financially)

Prof. Emily A. Carter,* Principal Investigator
Mr. De-en Jiang,* graduate student (Ph.D. June 2005)
Mr. Donald Johnson,* graduate student
Collaborator: Dr. Christopher J. Pickard (Accelrys, Inc.)

Inventions

Development of the following algorithms and codes:

- Ultrasoft spin-dependent pseudopotentials generated on-the-fly within the CASTEP planewave DFT code.